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EXTRACTION KINETICS MODELING OF AMARANTH SEED OIL SUPERCRITICAL FLUID EXTRACTION

KINETIČKO MODELOVANJE SUPERKRITIČNE EKSTRAKCIJE ULJA SEMENA AMARANTA

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ABSTRACT

Amaranth seeds contain oil with important nutritional properties, in particular, because of the presence of essential fatty acids, high content of minerals, vitamins, lysine and squalene. In this study, the kinetics of the supercritical fluid extraction of oil from three amaranth seed varieties has been investigated. The average oil content in amaranth seed was 58.2 g/kg, ranging from 54.6 to 61.1 g/kg depends on varieties, while squalene content ranged from 3.3 to 3.8 g/kg with an average content of 3.5 g/kg dry seed. Five empirical kinetic equations were successfully applied for kinetic modeling of extraction. As indicated by the appropriate statistical "goodness of fit" tests (such as the sum of squared errors, the coefficient of determination and the average absolute relative deviation), empirical models show good agreement with experimental data. The mathematical modeling of a process is beneficial to predict the process conduct and furthermore extend the procedures from laboratory to industrial scales.

Keywords: *amaranth seed oil, supercritical fluid extraction, kinetic modeling.*

REZIME

Ulja biljnog porekla danas privlače pažnju širom sveta zbog nutritivnog kvaliteta i zdravstvenih dobrobiti. Seme amaranta sadrži ulje sa važnim hranljivim svojstvima, posebno zbog prisustva esencijalnih masnih kiselina, visokog sadržaja minerala, vitamina, lizina i skvalena. Skvalen, nezasićeni triterpenski ugljovodonik, često se koristi kao sastojak funkcionalne hrane, dodatak ishrani ili potencijalni lek. U poređenju sa ostalim tehnikama ekstrakcije ulja, ekstrakcija superkritičnim fluidima nudi brojne prednosti, kao što su netoksičnost rastvarača, očuvanje životne sredine i ekstrakcija na relativno niskim temperaturama. U radu je proučena kinetika superkritične ekstrakcije ulja iz tri sorte semena amaranta. Ekstrakcija ulja je izvedena pri procesnim uslovima: pritisak od 300 bara, temperatura 40°C i protok CO_2 0,194 kg/h. U cilju proučavanja dinamike procesa ekstrakcije, vremenske sekvence ekstrakcije su postavljene na 30, 60, 90, 120, 150 i 180 min, s obzirom da je prinos dostigao ravnotežu nakon 3h za svaki od postupaka ekstrakcije. Prosečan sadržaj ulja u semenu amaranta iznosio je 58,2 g/kg, u rasponu od 54,6 do 61,1 g/kg u zavisnosti od sorte, dok se sadržaj skvalena kretao od 3,3 do 3,8 g/kg sa prosečnim sadržajem 3,5 g/kg. Glavni cilj rada je bio proučavanje kinetičkih aspekata superkritične ekstrakcije ulja modelovanjem krivih ekstrakcije. Za kinetičko modelovanje ekstrakcije uspešno je korišćeno pet empirijskih kinetičkih modela. Prema odgovarajućim statističkim karakteristikama (kao što su zbir kvadrata grešaka, koeficijent determinacije i prosečno apsolutno relativno odstupanje), empirijski modeli su pokazali dobro slaganje sa eksperimentalnim podacima. Matematičko modelovanje ekstrakcije ulja je značajno sa aspekta predviđanja odvijanja procesa, a takođe proširuje mogućnosti izvođenja postupka na industrijskom nivou.

Ključne reči*: ulje semena amaranta, superkritična ekstrakcija, kinetičko modelovanje.*

INTRODUCTION

Pseudocereals, like amaranth, quinoa and buckwheat, have been known as one of the favorite foods in the future, specifically because of their high protein content and absence of gluten (*Morales et al., 2020*). It has been reported that the protein, starch and oil of amaranth seeds are of high value of quality for food and feed use (*D'Amico and Schoenlechner, 2017*). Amaranth seed contains a high content of protein with a well-balanced profile of essential amino acids (*Taniya et al., 2020*).

Oils from plant/vegetable seeds are presently attracting worldwide consideration due to their nutritional quality and medical advantages (*Ergović-Ravančić et al., 2020*). Seed oil isolated from vegetable amaranth is an important source of natural bioactive compounds. Since the oil content in amaranth seed is about 5–9%, amaranth seed oil has received significance due to its unique fatty acids profile, high content of vitamins, amino acids, minerals and squalene (*Nasirpour-Tabrizi et al., 2020*). Amaranth seed oil extracts showed antioxidant, anti-inflammatory and anticancer potential (*Tang and Tsao, 2017*; *Yi et al., 2017*). A significantly greater amount of squalene (2.4–8.0%) was determined from amaranth seed oil in comparison to other plant oils like wheat germ, rice bran/husk and olive oils (*Cicero et al., 2018*). Amaranth seed was proposed to be a promising, natural plant source for the commercial production of squalene as another alternative to shark liver. Squalene, antioxidant triterpenes, has a few medical benefits including cardioprotective, hypolipidemic, hepatoprotective and antitoxicant activity (*Muzalevskaya et al., 2015*).

Some recently performed studies revealed that it is imperative to select the right extraction technique for optimal oil and squalene yield (*Krulj et al., 2016*; *Lozano-Grande et al., 2019*). In comparison with other oil methods of extraction, supercritical fluid extraction (SFE) offers various benefits such as being free from organic solvents, environment-friendly and operating at a medium range of temperature (*Wrona et al., 2017*). Oil separation from amaranth seed by supercritical CO_2 was investigated by *Wejnerowska et al. (2013)*. The authors mostly examined the optimization of material pretreatment, using the co-solvents as well as the process conditions, including extraction time, pressure, temperature and flow rate of carbon dioxide, etc. Several types of research have successfully used different mathematical models to fit oil extraction kinetics data of the numerous oils extracted from the different plant seeds (*Sánchez et al., 2018*; *Sodeifian et al., 2018*). A study by *Agu and Agulanna (2020)* was reported the kinetics and thermodynamics of amaranth seed oil separated by a conventional technique such as Soxhlet extraction. There is almost no published data on the results of the possible kinetic modeling amaranth seed oil extracted by SFE.

The mathematical modeling of the amaranth seed oil process extraction could be especially helpful since it provides a perception of the transport component to the extraction process. The kinetic models applied for assessment of the SFE kinetics should incorporate the empirical models, mass-transfer based models and models dependent on heat-transfer analog. The SFE mathematical modeling of a process is advantageous to predict the process conduct and also extend the procedures from laboratory to large-scale production. Therefore, the purpose of the current work was to study the kinetic aspects of supercritical CO_2 extracted amaranth seed oil by modeling the extraction curves.

MATERIAL AND METHOD

Material

The three amaranth varieties (Sample 1, 2 and 3) were cultivated in the field in Novi Sad, Serbia. Before extraction, seeds were milled using a laboratory mill (Knifetec 1095, Foss, USA).

Oil extraction and squalene determination

The supercritical CO_2 extraction of oil from amaranth seeds, as well as squalene determination by high-performance liquid chromatography, were performed according to methods described in the study of *Krulj et al., 2016*.

Extraction kinetics modeling

Five mathematical models used for amaranth seed oil SFE kinetics (*Table 1*) are usually utilized for this purpose and they are presented clearly elsewhere.

Statistical analyses

The data were processed statistically using the software package STATISTICA 12.0 (StatSoft Inc., Tulsa, OK, USA). All determinations were made in triplicate (n=3), all data were averaged.

RESULTS AND DISCUSSION

The content of all components extracted from the amaranth seed is influenced by their isolation procedure, as well as plant species and geographical origin. The oil content of three tested amaranth seed varieties ranged from 54.6 g/kg to 61.1 g/kg, with an average content of 58.2 g/kg dry seed (*Table 2*). These results are in accordance with the study of authors *Gimplinger et al. (2007)*, who considered that amaranth seed usually contains oil in an amount of about 50–80 g/kg. Squalene, an unsaturated triterpene component of amaranth seed oil, has acquired importance as a functional food, nutritional supplement, or potential drug. The values of squalene content varied from 3.3 to 3.8 g/kg dry seeds (*Table 2*). The obtained high squalene yield showed successful extraction by supercritical CO_2, an effective and eco-friendly method that excludes using large amounts of toxic solvent, long time extraction and additional purification process (*Papamichail et al., 2000*). Slightly lower squalene content in amaranth seed was observed in the study of *He et al. (2003)* who reported that the seed of *Amaranthus cruentus* contained 3.1 g/kg of squalene.

Table 2. The average yield of oil (during 180 min) and squalene extracted from amaranth seed

Oil yield (g/kg)			
Time (min)	Sample 1	Sample 2	Sample 3
15	4.20	6.90	5.40
30	14.3	17.9	16.0
60	31.9	36.3	34.2
90	46.3	50.9	44.8
120	53.0	56.2	49.4
150	56.8	58.0	53.2
180	58.8	61.1	54.6
Squalene (g/kg)	3.3	3.8	3.4

In general, it is necessary to model the extraction process for optimizing the factors and estimating the process of extraction. The SFE process in this study was conducted under the process conditions with a pressure of 300 bar, the temperature of 40 °C and CO_2 mass flow of 0.194 kg/h. In order to analyze the kinetics of extraction, oil yield was determined in samples removed every 30 min during 180 min. The results obtained from experimental data were fitted to the five generally used mathematical equations for the SFE modeling. Sum of squared errors (SSE), coefficient of determination (R^2) and average absolute relative deviation (AARD) were determined statistical

Table 1. Empirical models used for fitting of amaranth seed oil SFE kinetics data

No.	Model	Reference
Model I	$Y = Y_\infty \cdot \left(1 - e^{-k \cdot t}\right)$	*Brunner, 2013*
Model II	$Y = Y_\infty \cdot \left(1 - e^{(a \cdot t + b)}\right)$	*Reverchon and Sesti Osseo, 1994*
Model III	$Y = Y_\infty \cdot \frac{t}{k + t}$	*Papamichail et al., 2000*
Model IV	$Y = Y_\infty \cdot \left[1 - \left(f_1 \cdot e^{-k_1 \cdot t} + f_2 \cdot e^{-k_2 \cdot t}\right)\right]$	*Kandiah and Spiro, 1990*
Model V	$Y = Y_\infty \cdot G \cdot \frac{t}{t_1}$, for $t \leq t_1 = \frac{G}{K_m \cdot \dot{q}}$ $Y = Y_\infty \cdot \left[1 - (1 - G) \cdot e^{\frac{t - t_1}{t_i}}\right]$, for $t \geq t_1$	*Sovová, 2012*

Table 3. Statistical parameters applied for statistical "goodness of fit" tests (such (SSE, AARD and R^2) between experimental results and proposed models

Sample	Model I			Model II			Model III			Model IV			Model V		
	SSE	AARD	R^2	SSE	AARD	R^2	SSE	AARD	R^2	SSE	AARD	R^2	SSE	AARD	R^2
1	0.67	0.27	0.84	0.09	0.10	0.98	0.82	0.30	0.98	0.09	0.10	0.997	0.301	0.181	0.991
2	0.57	0.24	0.85	0.13	0.12	0.99	0.80	0.30	0.98	0.12	0.12	0.995	0.192	0.146	0.993
3	0.46	0.23	0.86	0.03	0.05	0.99	0.64	0.27	0.98	0.03	0.05	0.999	0.334	0.198	0.985

SSE - the sum of a squared estimate of errors; AARD - absolute average relative deviation; R^2 - coefficient of determination

Table 4. Calculated adjustable parameters of Models I-V used for modeling of SFE kinetics data

Sample	Model I		Model II			Model III		Model IV					Model V			
	Y_∞ (%)	k (min^{-1})	Y_∞ (%)	a	b	Y_∞ (%)	k (min^{-1})	Y_∞ (%)	f_1	k_1 (min^{-1})	f_2	k_2 (min^{-1})	Y_∞	G (min^{-1})	t_1	t_i (min^{-1})
1	7.19	0.01	6.53	-0.02	0.17	12.17	171.59	6.55	1.19	0.02	0.05	0.02	5.62	1.00	109.69	500.08
2	7.70	0.01	6.49	-0.02	0.16	10.70	120.32	6.49	1.18	0.02	0.03	0.05	6.11	0.96	101.29	500.89
3	6.44	0.01	5.77	-0.02	0.18	9.59	119.90	5.76	1.20	0.02	0.04	0.02	5.24	1.00	101.09	500.08

Y_∞ - total yield in infinite time of extraction process (%); k, k_1, k_2 - rate constant (min^{-1}); a - adjustable parameter;
b - correction factor; f_1, f_2 - extracted solute fraction; t_1- time constant extraction rate (min); t_i - time of internal mass transfer (min); G - parameter related to particle size and fragmentation

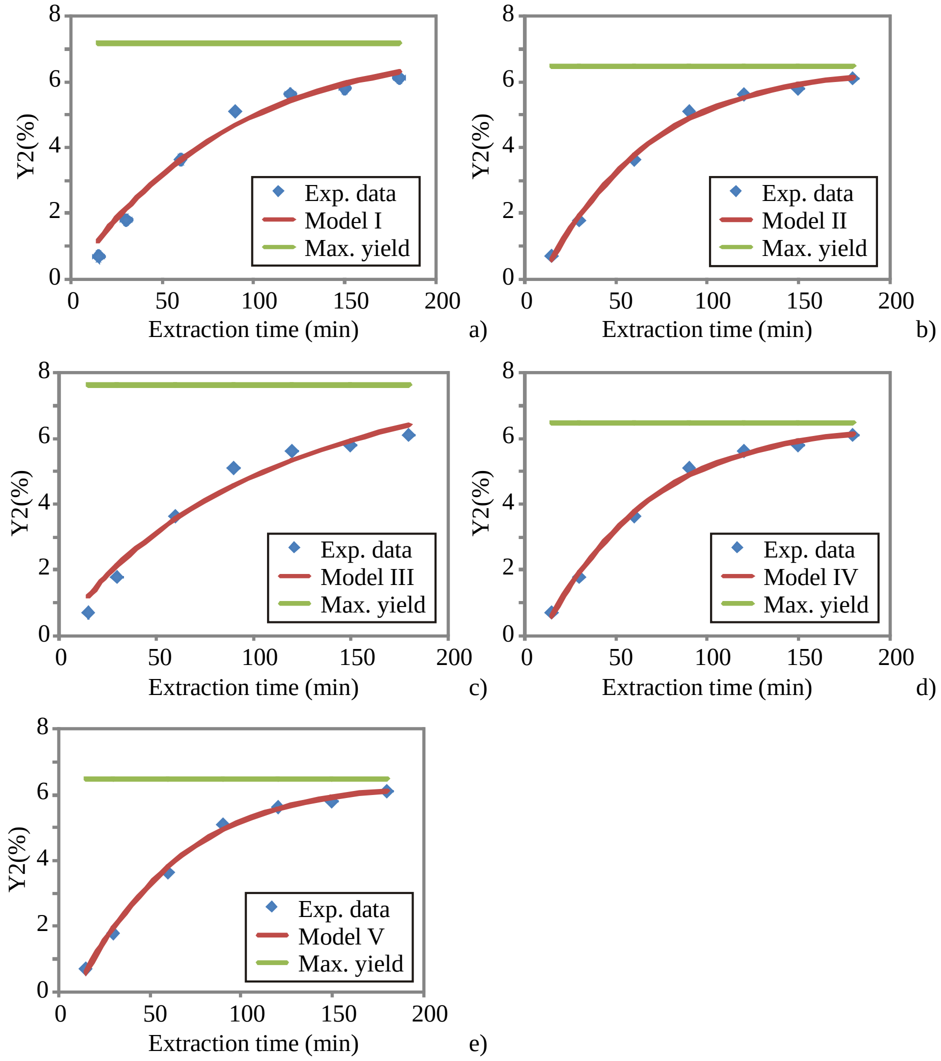

Fig. 1. Extraction curves with experimental and model data obtained for Models I-V (amaranth seed oil - sample 2)

experimental data and suggested models. Especially high values of R^2 and low SSE and AARD recommended satisfactory fit in case of all proposed mathematical models (*Table 3*). Nevertheless, Model IV gave a satisfactory quality of experimental and calculated data fit due to the highest R^2 as well as the lowest SSE and AARD (mean for all experiments: 0.997, 0.08 and 0.09, respectively). A comparative outcome was noticed in a recent study investigating wheat germ oil extracted by the SFE method (*Bojanić et al., 2019*). According to statistical features, Model I provided the weakest fit in comparison to other models.

The calculated parameters obtained from Model I, Y_∞ (total yield obtained for the infinite time of extraction process) and k (rate constant) were presented in *Table 4*. The parameter Y_∞ was in the range from 6.44 to 7.70%, while k was 0.01 min^{-1} for all samples. The highest value of Y_∞ was observed for sample 2, where the highest experimental global extraction yield was also obtained.

Model II presented slight changes from Model I, modified with the addition of parameter b (*Reverchon and Sesti Osseo, 1994). Y_∞* was in the range from 5.77 to 6.53%, while a was -0.02 min^{-1}. The highest Y_∞ was calculated for sample 1, while the highest parameter b was observed for sample 3.

Determined Y_∞ and k were generally the highest in Model III. The Y_∞ in Model III was in the range from 9.59 to 12.17%, while k was in the range from 119.90 to 171.59 min^{-1}. The highest Y_∞ and the highest k were determined for sample 1.

The extraction curve obtained for Model IV could be divided into two curves indicating fractions recuperated in solubility and diffusion controlled periods, separately. The sum of two divided curves for fractions f_1 and f_2, obtained from the total extraction curve for Model IV, was equivalent to extraction curves obtained from other models. The significantly high quantity of extracted oil was recuperated in solubility controlled period according to intensely higher f_1 (*Table 4*), which could be explained by a particularly high content of oil in amaranth seeds. Based on data from *Table 4*, it could be observed that Y_∞ was very similar for Models II and IV. The parameter Y_∞ in Model IV was in the range from 5.76 to 6.55%, f_1 was in the range from 1.18 to 1.20, f_2 was about 0, while k_1 and was 0.02 min^{-1} and k_2 was in the range from 0.02 to 0.05 min^{-1}.

Determined parameters from Model V proposed that the constant-extraction rate (CER- t_1) period ranged from 101.09 to 109.69 min. The quite long CER period in comparison to global extraction time was influenced by relatively high oil yield in samples. Parameter t_i which refers to the falling extraction rate (FER) period was amount 500.079 min (*Table 4*).

The FER period was longer than 180 min, proposing that the total extraction time applied in the experiment was not enough to completely extract oil from a plant seed. Nevertheless, the FER period is not so significant for the most of industrial SFE scale because the extraction processes would be finished almost immediately after the CER period (*Cavalcanti et al., 2016*). The most differences between measured and calculated parameters based on kinetics data for oil from three amaranth seeds indicate that plant varieties have a significant impact on the process of extraction regarding oil and squalene yield.

CONCLUSION

An underutilized plant source, such as amaranth seeds, could be used as a raw material for the extraction of valuable oil. From the green chemistry point of view, SFE is convenient as a productive and environmentally-friendly extraction method for amaranth seed oil. Amaranth seeds contain generally high content of squalene, a compound of high importance for application in various industries. The combination of the emerging technology of SFE and low-cost raw materials is an economical alternative to conventional extraction methods according to industry requests and sustainable development. Five empirical kinetic models were proposed for the modeling of the amaranth seed oil supercritical fluid extraction process. After statistical evaluation of these models, the most confident model was chosen to be a model with two separate curves, which describes solubility and diffusion controlled periods separately.

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